3. ALKALI METAL, AMMONIUM AND ALKALINE EARTH PERCHLORATES

AMMONIUM AND ALKALI METAL PERCHLORATES

The perchlorates of the Group I elements and ammonium perchlorate are white, crystalline solids. Thermochemical constants for these compounds are summarized in Table 3.1. All of the compounds except lithium perchlorate are dimorphic, exhibiting transitions from rhombic to cubic forms at the temperatures shown in Table 3.2. Crystal structures and magnetic susceptibilities are reported by Mellor.[1] Lithium perchlorate alone has a well-defined melting point. The others decompose upon melting or within a very short temperature range of the melting point.

Thermochemical data for the alkali metal perchlorates in solution are given in Table 3.3.

The heats of formation of the metal perchlorates are very nearly the same as the heats of formation of the corresponding chlorides. The reaction:

$$MClO_4 \rightarrow MCl + 2O_2$$

thus takes place with little net energy change. For this reason perchlorates, especially those of the light metals, are highly favored as solid oxidizers for rocket propellants. The oxygen content of the alkali metal perchlorates is given in Table 3.4. The oxygen in ammonium perchlorate is not all available for combustion of a fuel, however. Some must be used to burn the ammonium ion.

Marvin and Woolaver[47] studied the thermal decomposition of lithium, sodium and potassium perchlorates, among others, by means of the thermobalance. Their results verify that the decomposition yields the chloride and oxygen only in these three cases. Curves of weight loss *vs.* temperature for these compounds show a sharp break where decomposition begins, followed by a nearly isothermal region of decreasing weight.

Perchlorates are unusually soluble in organic solvents. Table 3.5 lists the solubilities of a number of perchlorates in a variety of solvents. Data for the first eight solvents were obtained by Willard and Smith.[92] The last three, for sodium and potassium perchlorates only, were measured by Isbin and Kobe.[35] The low solubility of potassium perchlorate in ethanol is the basis of one method for its analytical determination.

Molar, cationic and anionic magnetic susceptibilities have been determined for the Group I perchlorates[56] with the results shown in Table 3.6.

TABLE 3.1. THERMOCHEMICAL DATA FOR THE AMMONIUM AND ALKALI METAL PERCHLORATES

	$\Delta H^\circ_{f_{298}}$	$\Delta F^\circ_{f_{298}}$	$S^\circ_{f_{298}}$	C_p°	Solubility[a] g/100 g H_2O at 25° C	Density
NH_4ClO_4	−69.42				24.922	1.952
$LiClO_4$	−91.77				59.71	2.429
$NaClO_4$	−92.18				209.6	2.5357[b]
$KClO_4$	−103.6	−72.7	36.1	26.33	2.062	2.5298
$RbClO_4$	−103.87	−73.19	38.4		1.338	2.9
$CsClO_4$	−103.86	−73.28	41.89	25.71	2.000	3.327

[a] Willard, H. H. and Smith, G. F.[52]
[b] Fernández Alonso, J. I. and Gascó, L.[24]

TABLE 3.2. PHASE TRANSITION IN ALKALI METAL PERCHLORATES

Compound	Temp.	Transition
NH_4ClO_4	240[a, b]	Rhombic-cubic
$LiClO_4$	247[c]	Solid-liquid
$NaClO_4$	313[a], 308[b]	Rhombic-cubic
$KClO_4$	300[b]	Rhombic-cubic
$RbClO_4$	281[a], 279[b]	Rhombic-cubic
$CsClO_4$	224[a], 219[b]	Rhombic-cubic

[a] Gordon, Saul and Campbell, Clement.[27]
[b] Vorländer, D. and Kaascht, E.[58]
[c] Markowits, M. M.[46]

The electrical conductances at 25°C of aqueous solutions of lithium, sodium and potassium perchlorates were reported by Jones,[37] who calculated the limiting conductance of perchlorate ion to be 67.32 ± 0.06 conductance units. From measurements of the indices of refraction of solutions of perchloric acid and sodium and ammonium perchlorate, Mazzucchelli and Vercillo[53] deduced 6.66 ± 0.06 as the difference in molar refractive power between perchlorate ion and chloride ion. Mathias and Filho[48] measured the molar refractions of lithium and sodium chlorates and perchlorates and found that the molar refractions of chlorate and perchlorate ions as experimentally determined for various concentrations agree with the values predicted theoretically from the polarization of the electron pair and the oxygen ions in relation to positive centers of various field intensity.

Ammonium Perchlorate

Ammonium perchlorate is a colorless, crystalline compound with a density of 1.95 g/cc. The refractive indices of the crystal are 1.4824, 1.4828 and 1.4868.[94] The molar refraction is 17.22. It is prepared by a double displacement reaction between sodium perchlorate and ammonium chlo-

TABLE 3.3. THERMOCHEMICAL DATA FOR THE ALKALI METAL PERCHLORATES IN SOLUTION[47]

Compound	State	$\Delta H_f°_{298}$	$\Delta F_f°_{298}$	$S°_{298}$
NH_4ClO_4	in 500 H_2O	−63.2		
	∞ H_2O	−63.15		
$NaClO_4$	std. state, hyp. m = 1	−88.69	−65.16	57.9
	in 400 H_2O	−88.76		
	600	−88.73		
	1,000	−88.70		
	2,000	−88.68		
	5,000	−88.67		
	∞	−88.69		
	in CH_3OH	−94.6		
	in C_2H_5OH	−92.6		
$KClO_4$	std. state, hyp. m = 1	−91.45	−70.04	68.0
	in 500 H_2O	−91.580		
	600	−91.549		
	700	−91.532		
	800	−91.518		
	900	−91.507		
	1,000	−91.499		
	1,500	−91.474		
	2,000	−91.461		
	3,000	−91.447		
	4,000	−91.441		
	5,000	−91.437		
	8,000	−91.433		
	10,000	−91.433		
	20,000	−91.434		
	50,000	−91.438		
	100,000	−91.442		
	200,000	−91.444		
	500,000	−91.446		
	∞	−91.45		
$RbClO_4$	std. state, hyp. m = 1	−90.3	−70.02	73.2
$CsClO_4$	std. state, hyp. m = 1	−90.6	−69.98	75.3

TABLE 3.4. OXYGEN CONTENT OF THE ALKALI METAL PERCHLORATES

Compound	Weight Per Cent Oxygen
NH_4ClO_4	54.5
$LiClO_4$	60.1
$NaClO_4$	52.2
$KClO_4$	46.1
$RbClO_4$	34.6
$CsClO_4$	27.5

TABLE 3.5. SOLUBILITIES OF PERCHLORATES IN ORGANIC SOLVENTS, G/100 G SOLVENT AT 25°C[25, 92]

Cation	Solvent										
	Methyl Alcohol	Ethyl Alcohol	*n*-Propyl Alcohol	*n*-Butyl Alcohol	*i*-Butyl Alcohol	Acetone	Ethyl Acetate	Ethyl Ether	Ethylene-diamine	Monoetha-nolamine	Ethylene Glycol
Ammonium	6.862	1.907	0.3865	0.0170	0.1272	2.260	0.032	Insol.			
Lithium	182.25	151.76	105.00	79.31	58.05	136.52	95.12	113.72			
Sodium	51.355	14.705	4.888	1.864	0.786	51.745	9.649	Insol.	30.1	90.8	75.5
Potassium	0.1051	0.012	0.010	0.0045	0.0050	0.1552	0.0015	Insol.	2.81	1.36	1.03
Rubidium	0.060	0.009	0.006	0.002	0.004	0.095	0.016	Insol.			
Cesium	0.093	0.011	0.006	0.006	0.007	0.150	Insol.	Insol.			

TABLE 3.6. MAGNETIC SUSCEPTIBILITIES OF GROUP I PERCHLORATES ($\times 10^6$)[56]

Salt	Molar	Cationic	Anionic
NH_4ClO_4	46.3	18.0	28.3
$LiClO_4$	32.8	4.2	28.7
$NaClO_4$	37.6	9.2	28.4
$KClO_4$	47.4	18.5	28.9
$CsClO_4$	69.9	41.0	28.9

TABLE 3.7. THE SYSTEM H_2O-NH_4ClO_4[23]

Solid Phase	Temp. (°C)	Composition of Solution in Grams per 100 Grams	
		NH_4ClO_4	H_2O
NH_4ClO_4	0	10.74	89.26
NH_4ClO_4	25	20.02	79.98
NH_4ClO_4	45	28.02	71.98
NH_4ClO_4	60	33.64	66.36
NH_4ClO_4	75	39.45	60.55
NH_4ClO_4 + Ice	−2.7	9.8	90.2

ride[72] and crystallizes from water as the anhydrous salt. Phase relationships in the sodium chloride-ammonium perchlorate-water system are illustrated in this last reference. The salt has no known hydrates but forms a triammine which is unstable at room temperature.[79] Its solubility in liquid ammonia is 137.93 g/100 g NH_3 at 25°C.[34] The water solubility of ammonium perchlorate as determined by Freeth[23] is given in Table 3.7.

This reference contains complete data on ternary and quaternary equilibria in the system sodium perchlorate-ammonium sulfate-ammonium perchlorate-sodium sulfate-water at 60 and 25°C. A diagram of the reciprocal salt pairs at two temperatures is shown in Figure 3.1.

In view of the use of ammonium perchlorate as an oxidizer in rocket propellants, its thermal decomposition has been of considerable interest and has been studied extensively by Bircumshaw and coworkers.[7, 8, 10] He found that below 300°C the equation

$$4NH_4ClO_4 \rightarrow 2Cl_2 + 3O_2 + 8H_2O + 2N_2O$$

represented the major part of the products. Above 300°C the proportion of nitric oxide became appreciable and increasing, and above 350°C the equation[55]

$$10NH_4ClO_4 \rightarrow 2.5Cl_2 + 2N_2O + 2.5NOCl + HClO_4 + 1.5HCl + 18.75H_2O + 1.75N_2 + 6.375O_2$$

agrees well with the gas analysis. The nitric oxide reacts with the chlorine so that it was analyzed as nitrosyl chloride.

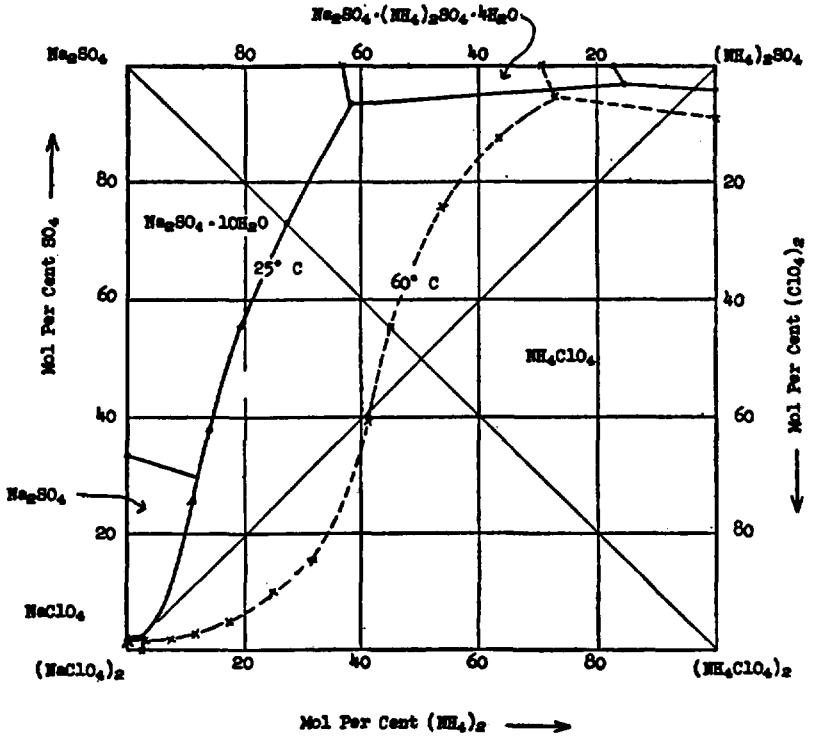

Figure 3.1. Jänecke diagram of reciprocal salt pair system. Na_2SO_4 — NH_4ClO_4 — $NaClO_4$ — $(NH_4)_2SO_4$ — H_2O at 25° and 60°C. (Freeth, F. A. [22])

It was found that below 290°C only 28 to 30 per cent of the salt decomposed, the residue being primarily undecomposed ammonium perchlorate. Exposure of this residue to water vapor "rejuvenated" it and upon further heating the decomposition would resume. Various other solvents were studied and the "rejuvenating" action was found to be proportional to the extent of solubility of the perchlorate in the solvent at 25°C.

Three separate activation energies have been observed for ammonium perchlorate decomposition. An activation energy of 29.6 kcal/mole was observed below 240°C, and 18.9 kcal/mole above 240°. This change coincides with the crystal transition from orthorhombic to cubic (see Table 3.2). In the 400 to 440°C temperature range the activation energy is 73.4 kcal/mole. At these higher temperatures sublimation is more rapid than is the solid phase decomposition and the large activation energy represents decomposition in the vapor phase. A region of poor reproducibility observed from 300 to 380°C is thought to be caused by the disruption of the crystal

surface by evaporation, breaking the reaction chains of the solid decomposition.

Gillespie[26] has made cryoscopic measurements on ammonium perchlorate in sulfuric acid and found an approximately threefold depression of the freezing point. He proposed that the reaction which takes place on dissolution can be represented as follows:

$$NH_4ClO_4 + H_2SO_4 = NH_4^+ + HClO_4 + HSO_4^-$$

The solutions were observed to fume in ordinary air, presumably due to the escape of free perchloric acid.

The density of solutions of ammonium perchlorate in water[50] and in aqueous perchloric acid[51] have been measured at 15 and 25°C. The conductivities of solutions of ammonium perchlorate in anhydrous hydrocyanic acid[14] and nitromethane[93] show agreement with the Debye-Hückel-Onsager equation. The dissociation constant of ammonium perchlorate in liquid ammonia solution[28] is 5.4×10^{-3}.

The Alkali Metal Perchlorates

Some confusion exists in the literature as to whether or not the alkali metal perchlorates possess well-defined melting points. Some handbooks[32, 42] list melting points for sodium and potassium perchlorates but not for the rubidium and cesium salts. Gordon and Campbell[27] listed melting points for all of the alkali metal perchlorates, obtained from an extensive differential thermal analysis study. This technique measures only heat effects, however, and the phenomena causing the effects must be determined by auxiliary observations. A thermogravimetric study by Marvin and Woolaver[47] revealed sharp breaks in the temperature-weight curves for sodium and potassium perchlorates at temperatures that correspond closely to the reported melting points. It is most probable therefore, that the liquids present at the observed melting points are eutectic compositions of the perchlorates and their decomposition products.

Lithium perchlorate melts at 247°C and does not begin to show an appreciable decomposition rate until the temperature is raised to over 400°C. This salt alone of the alkali metal perchlorates can thus be said to possess a well-defined melting point.

The trihydrate is the most common form of lithium perchlorate. The molar heat of hydration[78] is 14.2 kcal/mole and the water of hydration is extremely difficult to remove. Berglund and Sillen[5] found that some hydrate remained in a sample held at 300°C for 12 hours. Smeets[79] has identified three ammines of lithium perchlorate containing 2, 3, and 5 molecules of ammonia per molecule of salt.

Precise studies of the crystal structure of lithium perchlorate tri-

hydrate and the anhydrous lithium and potassium salts are reported.[61] From this work the precise geometry of the perchlorate ion was determined. Conductances and viscosities of some moderately concentrated solutions of lithium perchlorate in methanol-acetone at low temperatures were measured by Sears and co-workers.[73] Simmons and Rapp[76] measured the solubility of lithium perchlorate in water over the temperature range 0 to 172°C and the densities of the saturated solutions from 0 to 40°C. Densities of unsaturated solutions are reported by Mazzucchelli and Rossi.[52]

The solubility of lithium and silver perchlorates in a number of organic solvents and the spectra of acetone solutions of these salts have been reported by Pullin and Pollock.[60] Several of the absorption bands of acetone are observed to be split into two components in these solutions, and from the relative intensities of these components it is concluded that complexes of the type $Li^+(acetone)_2$ or $Ag^+(acetone)_2$ are present in solution. Diffusion coefficients[30] of lithium and potassium perchlorates and osmotic and activity coefficients[38, 65] of lithium and sodium perchlorates have been measured at 25°C.

Cryoscopic and conductivity measurements have been made on dilute solutions of lithium perchlorate in cyclohexanol,[41] which show the salt to be a strong electrolyte in this solvent. The conductivities of lithium and sodium perchlorate in methanol[16] and ethanol[17] have been measured by Copley and co-workers, and in ethanol and acetone by Koch and Frivold.[41] Walden and Hilgert[89] have reported conductivity values for lithium, sodium and potassium perchlorates in hydrazine while Coates and Taylor[13] studied these same salts in hydrocyanic acid. Wright, *et al.*[93] studied numerous perchlorates in nitromethane solution including the salts of ammonium, lithium and sodium. He found that plots of conductance against the square root of concentration show pronounced curvature in the region of low concentration, making extrapolation to infinite dilution very uncertain. The effect of lithium perchlorate on the mutual solubilities of water and *n*-butyl alcohol has been reported by Durand-Gasselin and Duclaux.[21]

Sodium perchlorate forms a tetrammine[79] and a monohydrate with a heat of hydration of 2.01 kcal/mole.[78]

Aqueous solutions of sodium perchlorate were studied extensively by Mazzucchelli and Pro[51] who also studied solutions of the salt in perchloric acid solutions and reported solubilities and apparent specific volumes of the salts. The system water-sodium perchlorate-sodium chloride was reported by Cornec and Dickely.[18] Osmotic and activity coefficients of sodium perchlorate solutions have been measured by Robinson and Stokes.[65] The Raman spectra of aqueous solutions have been reported.[63]

Refractometric measurements[94] showed the refractive indices of the crystal to be 1.4606, 1.4617 and 1.4731, and the molar refraction 13.58.

The electrical conductivity, dissociation and temperature coefficient of conductance from 0 to 65°C of aqueous solutions of sodium perchlorate were measured by Jones.[36] Liquid-junction potentials and the constancy of activity factors in sodium perchlorate-perchloric acid solutions were studied by Biedermann and Sillen.[6]

The aqueous mutual system from the perchlorate and nitrate salts of ammonia and sodium were studied by Karnaukhov,[39] as were the triple systems entering into this system: sodium nitrate-ammonium nitrate-water; ammonium nitrate-sodium perchlorate-water; sodium nitrate-sodium perchlorate-water; and sodium perchlorate-ammonium perchlorate-water. The solid phases separating from these systems were charactrized and were found to include, among others, the compound $7NH_4ClO_4 \cdot NaClO_4$ and several solid solutions. The isotherm of solubility of the system sodium perchlorate-ammonium perchlorate-water at 25°C is characterized by separation of three solid phases: NH_4ClO_4, solid solutions of $7NH_4ClO_4 \cdot NaClO_4$ in $NaClO_4$ and $NaClO_4 \cdot H_2O$.

The conductivity of the salt has been measured in methanol,[16] ethanol,[17] hydrazine,[89] hydrocyanic acid,[13] nitromethane[92] and dimethylformamide.[73]

An eutectic, melting at 310°C, in the system sodium perchlorate-barium perchlorate occurs at 43 mole per cent barium perchlorate.[96]

The use of a sodium perchlorate-acetyl chloride mixture in acetic anhydride has been found to be effective in the ring acetylation of phenol ethers.[49]

The refractive indices[94] of the potassium perchlorate crystal are 1.4717, 1.4724 and 1.476. The molar refraction is 15.37. Jones[36] measured the electrical conductivity, dissociation and temperature coefficient of conductance of aqueous solutions from 0 to 65°C. Activity coefficients were reported by Deno and Perizzolo.[19] Conductances of potassium perchlorate have been measured in dimethylformamide,[73] hydrogen cyanide[13] and hydrazine.[89]

Potassium perchlorate forms neither hydrates nor ammoniates. Solubility data[4] have been determined up to a temperature of 265°C. The system potassium chloride-potassium perchlorate-water has been studied at 150, 175, 200, 225 and 250°C and polytherms determined.[3] Solubilities in various salt solutions were determined by Bozorth.[11] The system potassium perchlorate-potassium fluoborate-water was studied by Ray and Mitra.[62]

Because of its high oxygen content and its inability to form hydrates, potassium perchlorate has found considerable use as an oxidizer in solid rocket propellants. Probably as an outgrowth of this use, the thermal decomposition of the salt has been studied quite extensively.

Simchen and co-workers[75] found that pure potassium perchlorate begins to decompose at 580°C. Bircumshaw and Phillips[9] studied the decomposi-

tion quite extensively and observed a weight loss at temperatures as low as 530°C. The reaction appeared to be quite complex and the reproducibility of the results was poor. Potassium chlorate and chloride were both produced during the decomposition, and it is likely that melting is associated with the formation of a eutectic mixture of reactant and products.

The kinetics of the isothermal decomposition of potassium perchlorate under its own evolved oxygen pressure was studied in a constant volume system by Harvey and co-workers.[81] They determined a phase diagram for the system potassium perchlorate-potassium chloride-potassium chlorate. By correlating kinetic data in the range 556 to 582°C, it was found that the decomposition proceeds by two first-order reactions. There is a solid-phase decomposition prior to the appearance of a liquid phase, and a liquid-phase decomposition which occurs after the melting of the sample is complete. The respective rates of these reactions are dependent upon the concentration of potassium perchlorate. The kinetic quantities found in this study are tabulated below:

Phase	E_a Kcal/Mole	A (Frequency Factor)	$\Delta S^\ddagger$ Cal/Mole-Deg
Solid	70.5 ± 0.4	2.36×10^{18}	0.6
Liquid	70.5 ± 0.4	1.31×10^{16}	8.6

A study of the isothermal decomposition of potassium perchlorate under constant oxygen pressure was made by Rodgers and Wassink.[66] These workers found that the rate is independent of oxygen pressure and first order in perchlorate in both solid and liquid phases. They proposed the following mechanism:

$$KClO_4 \rightarrow KClO_3 + \tfrac{1}{2}O_2 \text{ (rate-determining)}$$

$$KClO_3 \rightarrow \tfrac{3}{4}KClO_4 + \tfrac{1}{4}KCl \text{ (rapid)}$$

The kinetic constants are listed below:

Phase	E_a Kcal/Mole	A (Frequency Factor)	$\Delta S^\ddagger$ Cal/Mole-Deg
Solid	98.4 ± 10.5	1.8×10^{21}	36.6 ± 14.2
Liquid	80.7 ± 4.3	6.8×10^{17}	21.0 ± 5.8

The solid phase rate constants obtained in these two studies are equal at about 495°C, while the liquid phase constants are the same at about 543°C. The system is a difficult one to study and considerable scatter is observed in the experimental results.

The oxidation of carbon black by potassium perchlorate proceeds smoothly in the temperature range 320 to 385°C.[57] The reaction appears first order in each of the reactants with an activation energy of 40 ± 4 kcal. It is interesting that the activation energy is much lower than that for the decomposition of the perchlorate alone. Inhibition by potassium chloride is observed in the reaction with carbon black. Two rate equations

were found: one for the early, noninhibited portion of the reaction, and a second that holds in the later stages when the influence of potassium chloride becomes appreciable.

Extension of these studies to the reaction between potassium perchlorate and different forms of carbon[33] has revealed that the reaction is more complex than appeared previously. An empirical rate expression involving ⅓ powers is given. No theoretical explanation is given for the observed rate expression.

Aromatization of cyclic hydrocarbons by solid potassium perchlorate at temperatures in the range 350 to 380°C has been reported by Patai and Rajbenbach.[58] Excellent yields of naphthalene were obtained from tetralin by this method. Benzene, phenol and *m*-cresol were also obtained from, respectively, cyclohexene, cyclohexanol or cyclohexanone and 3-methylcyclohexanone, although in much poorer yields.

ALKALINE EARTH PERCHLORATES

Anhydrous perchlorates of the alkaline earth metals can be prepared by heating ammonium perchlorate with the corresponding oxides or carbonates.[84] Reaction takes place more rapidly and at lower temperature the more basic the metal.

Very little information has been reported about beryllium perchlorate. It has been prepared by the above method but no data concerning its physical or chemical properties have appeared in the literature.

Very little thermodynamic data has been published on the alkaline earth perchlorates. Heats of formation are reported for $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$[67] and estimated from heats of solution[78] and ionic heats of formation for $Ca(ClO_4)_2$ and $Sr(ClO_4)_2$. These values are given in Table 3.8.

None of the alkaline earth perchlorates have well-established melting points in the anhydrous state.

Endotherms were observed in a differential thermal analysis study[27] of magnesium and calcium perchlorate hydrates which may be associated with fusion or hydrate dissolution. Thermobalance studies[47] reveal that calcium perchlorate decomposes to calcium chloride in the same manner as the alkali metal perchlorates. Magnesium perchlorate hexahydrate, on the other hand, shows a gradual weight loss with no sharp break in the

TABLE 3.8. HEATS OF FORMATION OF THE ALKALINE EARTH PERCHLORATES

Compound	$\Delta H^\circ_{f,298}$	Compound	$\Delta H^\circ_{f,298}$
$Mg(ClO_4)_2$	−140.6	$Sr(ClO_4)_2$	−184 (est.)
$Ca(ClO_4)_2$	−178 (est.)	$Ba(ClO_4)_2$	−192.8

TABLE 3.9. SOLUBILITIES OF THE ALKALINE EARTH PERCHLORATES IN ORGANIC SOLVENTS, GRAMS PER 100 GRAMS SOLVENT AT 25°C[92]

Cation	Water	Methyl Alcohol	Ethyl Alcohol	n-Propyl Alcohol	n-Butyl Alcohol	i-Butyl Alcohol	Acetone	Ethyl Acetate	Ethyl Ether
Magnesium	99.601	51.838	23.962	73.400	64.366	45.497	42.888	70.911	0.2908
Calcium	188.60	237.38	166.24	144.92	113.54	56.961	61.860	75.623	0.2607
Strontium	309.67	212.01	180.66	140.38	113.49	77.87	150.06	136.93	insol.
Barium	198.33	217.06	124.62	75.654	58.168	56.226	124.67	112.95	insol.

TABLE 3.10. HYDRATES AND AMMONIATES OF THE ALKALINE EARTH PERCHLORATES

Compound	ΔH Formation* (kcal/mole adduct)	Compound	ΔH Formation
$Mg(ClO_4)_2 \cdot 2H_2O$	13.509[a]	$Sr(ClO_4)_2 \cdot 4H_2O$	13.2[b]
$Mg(ClO_4)_2 \cdot 4H_2O$	24.724[a]	$Ba(ClO_4)_2 \cdot 3H_2O$	8.63[b]
$Mg(ClO_4)_2 \cdot 6H_2O$	32.708[a]	$Mg(ClO_4)_2 \cdot 6NH_3$	99.1[c]
$Mg(ClO_4)_2 \cdot 6H_2O$	38.37[b]	$Ca(ClO_4)_2 \cdot 6NH_3$	72.6[c]
$Ca(ClO_4)_2 \cdot 4H_2O$	15.485[b]	$Sr(ClO_4)_2 \cdot 6NH_3$	64.9[c]
$Sr(ClO_4)_2 \cdot 2H_2O$	9.5[b]	$Ba(ClO_4)_2 \cdot 6NH_3$	54.3[c]

* ΔH formation from anhydrous salt and water or ammonia.
[a] Smith, G. F., Rees, O. W. and Hardy, V. R.[93]
[b] Smeets, C.[78]
[c] Smeets, C.[81]

temperature-weight curve. The product in this case is magnesium oxide. Another study[95] of the thermal decomposition of magnesium, calcium and barium perchlorates indicated that in the first case the final product is $(MgCl)_2O$. The calcium salt gives calcium chloride with traces of calcium oxide and barium perchlorate decomposes to barium chloride only.

The solubilities of a number of alkaline earth perchlorates in various solvents have been measured by Willard and Smith[92] and are shown in Table 3.9.

All of the alkaline earth perchlorates, with the possible exception of beryllium perchlorate, for which no data are available, form both hydrates and ammines. Heats of formation for a number of these have been measured and are given in Table 3.10. In addition to those tabulated the following ammines have been reported[81]:

$Mg(ClO_4)_2 \cdot 2NH_3$
$Ca(ClO_4)_2 \cdot 2NH_3$
$Ca(ClO_4)_2 \cdot 3NH_3$
$Sr(ClO_4)_2 \cdot NH_3$
$Sr(ClO_4)_2 \cdot 2NH_3$
$Sr(ClO_4)_2 \cdot 7NH_3$
$Sr(ClO_4)_2 \cdot 10NH_3$
$Sr(ClO_4)_2 \cdot 12NH_3$
$Ba(ClO_4)_2 \cdot 2NH_3$
$Ba(ClO_4)_2 \cdot 5NH_3$
$Ba(ClO_4)_2 \cdot 9NH_3$

The decammine and dodecammine of strontium perchlorate are unstable at room temperature. A reported heptammine of magnesium perchlorate is

probably the result of a typographical error and the existence of a tetrammine of calcium perchlorate has been disputed.[81, 85]

The heat of hydration of magnesium perchlorate in going from the anhydrous state to the hexahydrate is greater than the heat evolved by phosphorus pentoxide in going to orthophosphoric acid. This salt would thus be expected to be as efficient as phosphorus pentoxide as a drying agent, a fact which has been verified.[86] The great affinity of this salt for water is probably the cause of some dispute over its solubility in ethyl ether. Willard and Smith[92] reported a solubility of 0.29 g/100 g ether (Table 3.9). Later, Rowley and Seiler[68] reported a solubility of 0.06 per cent for this system, attributing the previous high value to the presence of moisture. A third value[5] of 20 to 25 per cent was published in 1948. Extreme care must be exercised to insure that both solvent and solute are anhydrous in working with magnesium perchlorate.

A trihydrate of magnesium perchlorate was reported by Willard and Smith[91] and disputed by Moles and Roquero,[54] who concluded that the supposed trihydrate was actually mixed crystals. Copeland and Bragg,[15] in an intensive investigation of the hydrates of this salt, found no evidence for the existence of a trihydrate. These workers measured aqueous vapor pressures for the equilibria

$$Mg(ClO_4)_2 \cdot 2H_2O + 2H_2O \rightleftharpoons Mg(ClO_4)_2 \cdot 4H_2O \qquad 8.15 \pm 0.54 \times 10^{-3} \text{ mm}$$

$$Mg(ClO_4)_2 \cdot 4H_2O + 2H_2O \rightleftharpoons Mg(ClO_4)_2 \cdot 6H_2O \qquad 20.9 \pm 1.1 \times 10^{-3} \text{ mm}$$

at 23°C. The vapor pressure of the saturated solution was found to be 81×10^{-3} mm and an upper limit of 0.56×10^{-3} mm was set for the equilibrium between the dihydrate and the anhydrous salt.

Mono-, di- and trietherates of magnesium perchlorate have been reported.[68] The salt is reported to have a high heat of solution and the monoetherate is stable above 100°C.

The solubility of magnesium, strontium and calcium perchlorates in water has been measured for the temperature range 0 to 50°C.[43] A linear relationship was found between temperature and solubility and between $\log \mu$ (where μ is the molar quantity) and $1/T$. Partial molar enthalpies and entropies were calculated from the slopes of the latter curves. Determination of pH values of aqueous solutions[2] of the alkali metal perchlorates showed that pH was a complex function of molality.

Magnetic susceptibilities of the alkaline earth perchlorates have been measured by Pacault and Stoltz[56] and are given in Table 3.11. Magnesium, calcium, strontium and barium perchlorates form hexapyridine complexes.[77] All of these except the magnesium compound are deliquescent, and it is highly hygroscopic.

Hydroxyperchlorates of magnesium, calcium and barium have been re-

TABLE 3.11. MAGNETIC SUSCEPTIBILITIES OF GROUP II PERCHLORATES ($\times 10^6$)[66]

Salt	Molar	Cationic	Anionic
$Mg(ClO_4)_2$	65.0	10.1	27.5
$Ca(ClO_4)_2$	70.5	16.0	27.2
$Sr(ClO_4)_2$	81.4	24.5	28.5
$Ba(ClO_4)_2$	94.7	38.2	28.3

ported by Hayek and Schnell.[29] These were formed by dissolving the metal oxides in the corresponding perchlorates. The pH, oxide content and absorption spectra of the resulting complex solutions were studied. The solid phases were identified as basic salts by x-ray analysis.

Aqueous solutions of all of the Group II perchlorates have been used as solvents for cellulose.[20, 22]

The preparation and properties of magnesium perchlorate and its use as a drying agent are reported in detail by Willard and Smith.[91] The Raman spectrum of monocrystals of magnesium perchlorate has been determined.[45, 90]

Bacarella and co-workers[2] studied the absorption of organic vapors by anhydrous magnesium perchlorate at 25°C. They found that methanol, ethanol, acetone, pyridine, acetonitrile, ammonia and nitromethane are all quantitatively absorbed by the salt. The absorption of 1,4-dioxane and chloroform was not quantitative. On this basis it is assumed that magnesium perchlorate could be a general reagent for polar vapors.

Tables of revised values for osmotic and activity coefficients of magnesium perchlorate were published by Stokes in 1948.[87]

Conductances of solutions of magnesium perchlorate have been measured in normal propyl and isopropyl alcohols,[70] methanol-acetone,[74] water,[71] and in acetone, methyl alcohol and nitromethane.[69] The conductances of acetone solutions of calcium perchlorate have also been measured.[69]

The basic calcium salts $3Ca(OH)_2 \cdot Ca(ClO_4)_2 \cdot 12H_2O$ and $Ca(OH)_2 \cdot Ca(ClO_4)_2 \cdot 2\text{-}4H_2O$ have been reported[40] and their crystal structures have been determined.[59]

Coefficients of adiabatic compressibility of aqueous solutions of calcium and strontium perchlorates have been reported.[25] Conductances of solutions of strontium perchlorate in methanol-acetone have been measured.[74]

The preparation of barium perchlorate trihydrate and its use as a desiccant have been described by Smith.[88] Refractometric measurements of crystals of the trihydrate[94] show the refractive indices to be 1.533 and 1.532 and the molar refraction 41.60.

Preparation of the anhydrous salt and its use as a drying agent and ammonia absorbent have been described.[82] The barium amino perchlorates

TABLE 3.12. DISSOCIATION PRESSURES OF BARIUM AMMINO PERCHLORATES[80]

Equilibrium System	Pressure of Ammonia (mm)							
	−79°C	−21.5°C	0°C	20°C	40°C	60°C	75°C	80°C
$Ba(ClO_4)_2$-$Ba(ClO_4)_2 \cdot 2NH_3$			4	8	20	54	106	130
$Ba(ClO_4)_2 \cdot 2NH_3$-$Ba(ClO_4)_2 \cdot 5NH_3$		4	16	60	182			
$Ba(ClO_4)_2 \cdot 5NH_3$-$Ba(ClO_4)_2 \cdot 6NH_3$		28	64	125	190			
$Ba(ClO_4)_2 \cdot 2NH_3$-$Ba(ClO_4)_2 \cdot 6NH_3$						434	780	
$Ba(ClO_4)_2 \cdot 6NH_3$-$Ba(ClO_4)_2 \cdot 9NH_3$	2	120	390					

have been studied extensively by Smeets,[80] who measured the equilibrium dissociation pressures at several temperatures, as shown in Table 3.12.

The electrolysis of barium perchlorate has been studied in several organic solvents and its conductance measured in furfural, "Cellosolve" and ethylene glycol.[12]

Anhydrous barium perchlorate shows two crystal transitions, $\alpha \rightarrow \beta$ at 284°C and $\beta \rightarrow \gamma$ at 360°. It forms a eutectic melting at 310°C with sodium perchlorate.[96] The eutectic occurs at 43 mole per cent barium perchlorate. The basic salt $Ba(OH)ClO_4$ has been reported.[64]

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